Surface Water and Sediment Monitoring Study for Methoxyfenozide

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Classification:	This study is classified as supplemental, non-guideline.
PC Code:	121027
Reviewer:	Karen Milians, Ph.D., Chemist Chuck Peck, Environmental Engineer

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Executive Summary

Methoxyfenozide (CAS No. 161050-58-4; PC Code 121027) is a registered insecticide (insect growth regulator) for a variety of agricultural as well as non-agricultural uses. In 2000, methoxyfenozide was initially issued a conditional registration due to uncertainties associated with the environmental fate and effects of the chemical. Because methoxyfenozide is very persistent, moderately mobile and expected to accumulate in the environment following repeated applications, the Agency was concerned regarding accumulation to significant levels in water and in benthic sediments. Therefore, a surface water and sediment monitoring study was recommended using a representative sample of water bodies in high use areas (based on DAS record sales, growers and state and county government records) to determine whether multiple years of use would result in accumulation of methoxyfenozide residues in water and/or sediment. Samples of methoxyfenozide residues were collected over a two-year period (2012 and 2013) in two lotic (flowing) water bodies (*e.g.* rivers) and five lentic water bodies (*e.g.* ponds) in each of the following states: California, Mississippi, and Michigan. The review for the selection of these sites is documented in the following USEPA memos: DP Barcodes 394308, 398763, and 400676.

Surface water samples were collected four times daily at all lotic sites by an automated sampler and composited into 7-day samples. Four consecutive 7-day composites were mixed into 28-day composites by the analytical laboratory. Grab sampling methods were used for lentic water sampling events and for lotic and lentic sediment sampling events. Transit stability and control sample studies were conducted for each study area and were analyzed in concurrence with field samples. Recoveries ranged between 81 to 93% for water and 67 to 99% for sediment samples.

Analytical method performance (method validation) for concurrent fortification samples for water ranged from 61 to 116% and ranged from 74 to 128% for sediment. The analytical method [high performance liquid chromatography couple with mass spectrometer (tandem)] was deemed acceptable by the study authors for routine use on water and sediment, with a limit of quantitation

(LOQ) of 0.050 µg/L for water and 10.0 µg/kg for sediment; and a limit of detection (LOD) of 0.015 µg/L for water and 3 µg/kg for sediment.

The maximum concentration of methoxyfenozide in lotic surface water was found in Mississippi with a 1.31 µg/L and for a lentic watershed the maximum concentration of 0.845 µg/L was obtained in Michigan. No apparent accumulation of methoxyfenozide was observed in surface water in both lentic and lotic sites. The sediment results indicate that methoxyfenozide is not likely to accumulate in sediment. The maximum concentration of methoxyfenozide in sediment (31 µg/kg) was found in Michigan.

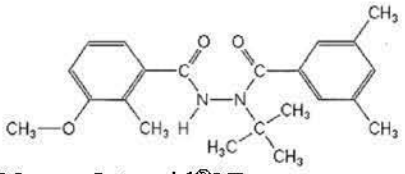
Table 1. Results Synopsis

Site	Concentration of methoxyfenozide in surface water (µg/L), (Number of samples analyzed)		Concentration of methoxyfenozide in sediment (µg/kg), (Number of samples analyzed)	
	Lotic	Lentic	Lotic	Lentic
California	ND-1.01 (88)[1]	ND-0.0502 (20)	ND (8)	ND (20)
Mississippi	ND-1.31 (55)[2]	ND-0.233 (20)	ND (8)	ND (20)
Michigan	ND (36)[3]	ND-0.845 (23)	ND (4)	ND-31.0 (23)

LOQ=0.050 µg/L and LOD= 0.015µg/L in surface water and LOD= 3 µg/kg in sediment.
ND =below detection limit
[1]87, 7- day composite samples and 1, 28-day composite sample
[2]47, 7- day composite samples and 8, 28-day composite samples
[3]22, 7- day composite samples and 14, 28-day composite samples

I. Materials and Methods

A. Materials:



1. Test Material: Product Name: Intrepid®2F
Formulation Type: suspension concentrate
CAS #: 161050-58-4
Storage stability: Transit stability and control sample studies were conducted annually for each study area (2012-2013). For fortified surface water samples the recoveries ranged from 81%-91% whereas for sediment the recoveries ranged from 67%-96%.
Characterization was not part of the study as the local growers used the formulation product.

2. Storage Conditions: Ambient temperature.

B. Test Sites:

Test sites are provided in **Table 2**. EFED had reviewed the data submitted by DAS regarding these sites and found them acceptable for the surface water and sediment monitoring study (DP Barcodes 394308, 398763, and 400676). The reviewer noted changes in one sampling site in Michigan because the landowner filled the pond (MILE06) and therefore, an alternate sampling point was selected (MILE07).

Table 2. Field Study Sites[1]

States	Counties	Site ID	Site type	Water Body
California	Fresno	CALE04	Lentic	San Joaquin River
	Kings	CALE05	Lentic	San Joaquin River
	San Joaquin	CALO01	Lotic	N. Fork S. Little Johns Ck.
		CALO02	Lotic	Temple Creek
		CALE01	Lentic	San Joaquin River
		CALE02	Lentic	San Joaquin River
	Stanislaus	CALE03	Lentic	San Joaquin River
Michigan	Berrien	MILO01	Lotic	Hickory Creek
		MILE01	Lentic	Runoff Pond
		MILE02	Lentic	Runoff Pond
		MILE03	Lentic	Runoff Pond
		MILE04	Lentic	Runoff Pond
		MILE05	Lentic	Runoff Pond
		MILE06	Lentic	Runoff Pond
		MILE07	Lentic	Runoff Pond
Mississippi	Tallahatchie	MSLO01	Lotic	Black Bayou
		MSLO02	Lotic	Black Bayou
		MSLE01	Lentic	Swan Lake
	Bolivar	MSLE02	Lentic	Pond
	Washington	MSLE03	Lentic	Tailwater Recovery
		MSLE04	Lentic	Drainage Ditch
	Humphreys	MSLE05	Lentic	Drainage Ditch

[1]From the study report page 47.

Site Selection Process and Description

According to the criteria for the monitoring study, vulnerable watersheds were selected that have a history of methoxyfenozide use (5-10 years use, based on DAS record sales, growers and state and county government records) and soils prone to runoff (hydrologic group C and D).

California

California was selected for monitoring because it leads the country in Intrepid®2F sales. The selected lotic monitoring sites were in San Joaquin County, the fifth highest Intrepid®2F sales county in the US. The selected lentic water body sites were in and downstream of Fresno, King, Stanislaus and San Joaquin counties. The surface water and sediment samples in these areas

were characterized and can be found in **Table 3** and **Table 4**, pages 50-51, respectively of the study report.

Michigan

The use of methoxyfenozide in Michigan has steadily decreased since 2006. Methoxyfenozide use on blueberries resulted in a significant increase in sales in 2008; however, the soils for this type of use had low runoff potential and the 5-10 years of historical use were not available. As a result, DAS focused their site selection on the grape production in southwestern Michigan. In terms of lotic sites, only the Hickory Creek was selected, despite the fact that the use data available from growers is limited to 4 years. The selected lentic sites are vineyards near Garr and Grange Roads, West Hinchman Road, E Lemon Creek Road, Burgoyne Road and Marrs Road. One sampling site was changed because the landowner filled the pond (MILE06) and therefore, an alternate sampling point was selected (MILE07). The surface water and sediment samples in these areas were characterized and can be found in **Table 3** and **Table 4**, pages 50-51, respectively of the study report.

Mississippi

The volume of methoxyfenozide use was greatest in Mississippi during the period 2007-2010. Selected lotic water sampling sites in Tallahatchie County, MS were monitored on Black Bayou along with a lentic sampling site on a nearby lake. Four additional lentic sampling sites were monitored: a pond in Bolivar County; a tailwater recovery pond and a drainage ditch in Washington County; and, a drainage ditch in Humphreys County. The surface water and sediment samples in these areas were characterized and can be found in **Table 3** and **Table 4**, respectively (pages 50-51 of the study report).

Table 3. Surface Water Characterization

Parameter	Value
Site 1 : California	
pH range	**7.7-8.7**
Hardness (mg equivalent $CaCO_3$/L)	**12-421**
Turbidity	**3.85-55.9**
Site 2 : Michigan	
pH range	**7.5-8.9**
Hardness (mg equivalent $CaCO_3$/L)	**17-354**
Turbidity	**0.91-63.2**
Site 2 : Mississipi	
pH range	**7.5-8.5**
Hardness (mg equivalent $CaCO_3$/L)	**40-119**
Turbidity	**6.83-606**

Table 4. Sediment Characterization at the sites

Sites	USDA Textural Class	%Sand	%Silt	%Clay	Cation Exchange Capacity (meq/100g)	% Organic matter	pH in 1:1 Soil:water Ratio	Redox potential @ 20.0 °C & pH 7.1
California Samples	Sand	91	6	3	6.6	0.33	7.1	185
	Sandy Clay Loam	55	24	21	14	1.2	7.2	140

Sites	USDA Textural Class	%Sand	%Silt	%Clay	Cation Exchange Capacity (meq/100g)	% Organic matter	pH in 1:1 Soil:water Ratio	Redox potential @ 20.0 °C & pH 7.1
	Sand	93	6	1	3.8	0.07	7.3	202
	Sandy Loam	69	20	11	8.2	1.03	7.8	183
	Sand	87	10	3	4.8	0.28	8.0	146
	Sand	95	4	1	2.6	0.46	6.8	207
	Loamy Sand	85	10	5	5.0	0.94	7.1	157
Michigan Samples	Sand	88	8	4	6.0	1.4	7.9	236
	Sand	90	6	4	4.9	0.97	7.7	200
	Loamy sand	82	10	8	10.5	3.2	7.9	169
	Sandy Loam	70	16	14	5.9	1.4	6.7	298
	Sandy Clay Loam	52	22	26	12.4	1.2	7.8	227
	Silty Clay Loam	12	60	28	8.9	6.6	5.9	305
	Clay	16	40	44	10.1	14.0	5.8	276
	Sand	88	10	2	6.8	3.3	7.0	72
Mississippi	Silty Clay Loam	18	54	28	12.3	3.4	5.6	342
	Clay	22	28	50	22.0	3.8	6.7	311
	Clay	24	18	58	21.1	17.6	5.4	325
	Clay	38	16	46	29.6	3.2	6.5	266
	Clay	32	10	58	34.0	2.6	7.3	191
	Clay	34	8	58	33.9	3.9	6.5	262
	Clay	26	20	54	26.1	3.4	6.4	248

C. Experimental Design:

Field Treatment/Application-Commercial formulations of Intrepid®2F were applied by local growers and were not controlled as part of this study.

D. Sampling:

Automated samplers were installed at each site (lotic sites). Using a peristaltic pump, drew surface water from a tubing installed near the bottom of the stream bed.

Lotic sites

Surface water in lotic sites was collected by extending a section of intake tubing from the stream to the autosampler, which was placed nearby in a protective steel box. Surface water was collected four times daily at all lotic sites by an automated sampler into 7-day composite samples. Four consecutive 7-day composites were mixed into 28-day composites. The 28-day composites were from the non-widespread use period for each state. The sample volume collected was approximately 50mL of surface water. These daily water samples were then deposited into a

2000mL high density polyethylene (HDPE) bottle which resulted in a weekly composite, then subsampled into a 250 mL bottle and shipped chilled to the analytical laboratory. The frequency of site visits for sample retrieval was weekly for the first four weeks of sampling then once every 14 days.

Additionally, the sampling stations contained a temperature sensor that allowed the recording of the temperature at each sampling event. This information was then transmitted electronically to Waterborne.

Sediment was collected on four occasions over the two use seasons monitored. In CA, samples were collected in April (the start of the widespread use period) and in November (the month following the end of the widespread use period). In MS and MI, the samples were collected two months before and after the widespread use period, (May and October in MI and April and October in MS).

Lentic Sites

Surface water and sediment samples were collected with grab sampling techniques. Surface water was collected before sediment samples by submerging a sample bottle below the water's surface, allowing it to fill, and then removing it for labeling, packaging and shipment. Sediment was collected with a clean hand tool from sediment's surface to a depth of one inch. Three locations in close proximity were sub-sampled, and the subsamples composited to create a single, composite sample.

Precipitation Monitoring

Precipitation in the form of rainfall was obtained for each watershed from the Next-Generation Radar (NEXRAD) system operated by the National Weather Service, an agency of the National Oceanic and Atmospheric Administration (NOAA). Precipitation was calculated for each watershed using NEXRAD data, while stage data were monitored at each lotic site. In California, 2012 was a normal precipitation year (13.57 inches) with rainfall measured at 98% of the 30-year normal. However, in 2013 precipitation (4.61 inches) only reached 33% of the 30-year normal.

In Michigan, precipitation in 2012 (33.76 inches) and 2013 (27.21 inches) was 91% and 79%, respectively, of the 30-year normal. In Mississippi, precipitation in 2012 (44.27 inches) and 2013 (58.40 inches) was 81% and 107%, respectively, of the 30-year normal.

In all sites, increases in stage were associated with precipitation events and confirm the potential for runoff to enter the streams from the methoxyfenozide use areas. In California, changes in stage that occurred during minimal rainfall events were the result of the movement of irrigation water through the stream during the growing season.

Control and Transit Stability Sampling Procedures

Transit stability samples were prepared with subsamples of bulk surface water and sediment collected from water bodies near sampling points in each State, but away from methoxyfenozide use areas. Three transit stability replicates of both surface water and sediment were fortified at low (0.25 µg/L) and at high concentration (1.0 µg/L). A total of 36 fortified samples were collected

over the entire study (18 surface water and 18 sediment samples).

Three unfortified surface and three unfortified sediment control samples were collected each year (a total of 12 control samples). These samples were prepared by the laboratory and sent with the transit stability samples to each State during each transit stability sampling event.

E. Analytical Procedures:

Water samples were analyzed according to the analytical method described by DAS method 110356 (Shackelford, D. 2012). It was noted by the reviewer that this method was different than the Environmental Chemical Method (ECM) for water submitted to the Agency and described in MRID 47824201.

Methoxyfenozide was extracted from water using 1N hydrochloric acid. An aliquot of the extract was then purified using solid phase extraction (SPE) cartridge. The SPE cartridge was washed with a water:methanol:formic acid (60:40:0.1) solution and then eluted with acetonitrile (ACN). The eluate was evaporated to dryness and reconstituted with water:acetonitrile:formic acid (70:30:0.05), then analyzed using high performance liquid chromatography (HPLC) with tandem mass spectrometry (LC/MS/MS, Applied Biosystems/Sciex API 4000 LC/MS/MS system). The study author noted the following deviation: all preparations of the water:acetonitrile:formic acid were made incorrectly with water:acetonitrile:formic acid (70:30:0.05), instead of 70:30:0.1 ratio as previously documented in the analytical method. The limits of detection (LOD) for the water samples was 0.015 µg/L and the limit of quantitation (LOQ) was 0.050 µg/L.

Sediment samples were analyzed according to the method described by DAS Method 110354 (Shackelford, D. 2012). It is noted however, that this method differs from the ECM submitted to the Agency for soil and sediment and described in MRID 47809902.

Methoxyfenozide was extracted from sediment samples using a methanol:0.1N hydrochloric acid solution (90:10). An aliquot of the extract was diluted with water and purified using a SPE cartridge. The cartridge was then washed with a water:methanol:formic acid (60:40:1) solution and eluted with ACN. The eluent was evaporated to dryness and the residues were reconstitute in water:ACN:formic acid (70:30:0.05) and then analyzed using HPLC/MS/MS. The LOD for the sediment samples was 3 µg/kg and the LOQ was 10.0 µg/kg.

HPLC/MS/MS conditions for both water and sediment samples

The column used was a Phenomenex Luna C18(2) HST. A combination of solvents were used as the mobile phase (0.1% formic acid in water and ACN) with a flow rate of 1000 µL/min (refer to page 128 of the study report for gradient details). The ionization mode was turbo spray with a positive polarity.

F. Verification of the Extraction Method and Storage Stability:

1. Spike Recoveries:

Individual sample recoveries for control and fortified samples in water and sediment ranged from 82 to 142% and from 81 to 112%, respectively. Most of the recoveries were within the acceptable range of 70 to 120%, with the exception of one water recovery at the 0.050 µg/L fortification level (142%, no explanation was obtained in the report regarding the high recovery). Therefore, the analytical methods were deemed acceptable by the study authors for routine use on water and sediment, with a limit of quantitation (LOQ) of 0.050 µg/L for water and 10.0 µg/kg for sediment, and a limit of detection (LOD) of 0.015 µg/L for water and 3 µg/kg for sediment (refer to Table 3-Table 6, pp. 152-159 of the study report).

Table 5. Summary of Method Verification Recoveries from Fortified Controls in Water and Sediment.

Fortified Concentration	Number of samples	Range (%)	Mean recovery (%)	Std. Dev.
Water				
Method Verification				
0.05 µg/L	12	90-142	108	15
1.0 µg/L	9	82-111	94	11
Total	21	82-142	102	14
Concurrent Recovery (method validation)				
0.05 µg/L	55	68-116	90	11
1.0 µg/L	35	61-112	90	12
1.5 µg/L	1	89	N/A	N/A
Total	91	61-116	90	11
Sediment				
Method Verification				
10.0 µg/kg	9	85-109	95	7
1000 µg/kg	9	81-112	92	11
Total	18	81-112	94	9.2
Concurrent Recovery (method validation)				
10.0 µg/kg	11	74-120	91	16
1000 µg/kg	15	77-128	95	14
Total	26	74-128	93	15

This table was obtained from the study report page 160.

Analytical method performance (method validation) was documented for each analytical set by analyzing concurrently laboratory fortified control samples and field samples. Average concurrent fortification recoveries for water ranged from 61 to 116% and the average concurrent fortification recoveries for sediment ranged from 74 to 128%. No explanation regarding the low recoveries in water for two samples was provided in the study report.

Transit stability samples from each location site were also analyzed concurrently with the field samples. Recoveries ranged between 81 to 93% for water and 67 to 99% for sediment samples (refer to **Tables 10** and **11** pp. 175-178 of the study report). According to the study authors, the recoveries indicate no significant degradation of methoxyfenozide occurred during handling and storage of samples at the field sites.

2. **Storage Stability Study:**

After sample collection, samples were placed on blue ice or wet ice and shipped overnight to ABC laboratories, Columbia, MO. Samples were then processed for analysis or stored in temperature

monitored refrigerators (water) and freezers (sediment).

The maximum storage interval evaluated during the storage stability analysis for water showed fortified control water samples to be stable in refrigerator storage for 180 days (see p. 179 of the study report). The longest refrigerator storage interval between the times the water samples were collected in the field and sample extraction at ABC Laboratories, Inc. was 147 days.

The maximum storage interval evaluated during the storage stability analysis for sediment showed fortified control sediment samples to be stable in frozen storage for 197 days (see p. 180 of the study report).The longest frozen storage interval between the times the sediment samples collected in the field and sample extraction at ABC Laboratories, Inc. was 137 days.

Table 5. Storage stability of water and sediment

Media	Storage Stability Study (days)	Maximum storage interval for samples (days)
Water at 4°C	180	147
Sediment (frozen)	197	137

II. Results and Discussion

A. Sales Data for 2012 and 2013:

California

The use and sales data were obtained from the California Pesticide Use Reporting (PUR) Program of the California Department of Pesticide regulation and the Office of the Agricultural Commissioner (OAC of San Joaquin County). In 2012, use records provided by the OAC indicate 1,036 lbs a.i. were applied in the CALO01 watershed, a 4-fold increase in lbs a.i. from the 252.4 lbs a.i. applied in 2011. In 2013, the use in CALO01 dropped to 892 lbs a.i.. In the CALO02 watershed, the 2012 use was 1,600 lbs a.i., greater than 2-fold increase from the 2011 use of 688.4 lbs a.i.. The 2013 use in CALO02 increased slightly over the 2012 use to 1,630 lbs a.i..

In lentic sites counties with discharge upstream of the San Joaquin River monitoring sites presented an increase in sales from 2012 to 2013 in all counties (Fresno, Madera, Merced, Stanislaus and San Joaquin). In 2012, a total of 13,182 lbs a.i. were sold, and in 2013 a total of 19,248 lbs a.i. were sold by DAS. Similarly, upstream of the Kings River monitoring sites a total of 67,228 and 106,506 lbs a.i. were sold in 2012 and 2013, respectively.

Michigan

Most of the use results were obtained from grower records. A large increase in applications between 2010 and 2011 (from 67.9 lbs a.i. to 313.4 lbs a.i.) was observed, followed by a decrease to 114.3 lbs a.i. in 2012. In the study this decline was attributed to weather damage (loss from

freezing conditions). The use in 2013 (288.9 lbs a.i.) nearly returned to the level of use in 2011 (313.4 lbs a.i.).

Mississippi

Limited applications of methoxyfenozide were made during the two growing seasons monitored in Mississippi near the two lentic monitoring sites. In the fields surrounding the lotic sites and the MSLE01 site, applications to corn were made in both 2012 and 2013. Approximately 32.9 lbs a.i. were applied in two of the growers blocks and 54.4 lbs a.i. were applied to five of the growers blocks. In 2012, an application of 14.2 lbs a.i were made in two blocks at MSLE04.

B. Findings:

Lotic Sites

In California, the methoxyfenozide concentration for the single 28-day composite sample collected at CALO01 site was reported at 0.589 µg/L (Table 15 pp.60-62 of the study report). The methoxyfenozide concentrations for 26 of the 7-day composite samples ranged from 0.0607 µg/L to 0.813 µg/L and 42 of the 7-day composite samples were reported at concentrations below the LOQ (0.050 µg/L) and above the LOD (0.015 µg/L). Nineteen of the samples were reported below the LOD.

Similarly, the methoxyfenozide concentration for the single 28-day composite sample collected at CALO02 was reported at 0.212 µg/L. The methoxyfenozide concentrations for 64 of the 7-day composite samples ranged from 0.0502 µg/L to 1.01 µg/L and 21 of the 7-day composite samples were reported at concentrations below the LOQ and above the LOD. One of the 7-day composite samples was reported below the LOD.

All 28-day (14 in total) and all 7-day composite (22 in total) surface water samples collected at the Michigan lotic site were reported below the LOD.

In Mississippi, the methoxyfenozide concentration for the single 28-day composite from MSLO01 collected before the beginning of the widespread use period was reported below the LOQ and above the LOD. The methoxyfenozide concentrations for six of the seven 28-day composite samples collected at MSLO01 between the 2012 and 2013 widespread use periods were reported below the LOQ and above the LOD. The 28-day composite from MSLO01 collected immediately after the end of the 2012 widespread use period was reported at a concentration of 0.0588 µg/L. None of the 7-day samples collected after the end of 2013 widespread use period from MSLO01 were selected for compositing into a 28-day sample, all 7-day samples were analyzed individually.

For the 7-day composite samples (47) collected at MSLO01 and analyzed individually, six were reported below the LOD and 20 were reported below the LOQ and above the LOD. Of the remaining 21, 7-day composite samples, four collected during the fall of 2012 (9/30 - 10/27/12), were reported at concentrations ranging from 0.0628 µg/L to 0.0917 µg/L. Seventeen that were collected from mid-summer ((beginning 7/7/13) through the fall of 2013 (11/2/13) were reported at concentrations ranging from 0.176 µg/L to 1.31 µg/L.

The methoxyfenozide concentration for the single 28-day composite sample collected at MSLO02 before the beginning of the 2012 widespread use period was reported below the LOD. The methoxyfenozide concentration for five of the seven 28-day composite samples collected at MSLO02 between the 2012 and 2013 widespread use periods were reported below the LOQ and above the LOD. The two remaining 28-day composite samples collected at MSLO02 between the 2012 and 2013 widespread use periods were reported at a concentration of 0.0531 µg/L (12/23/12 - 1/19/13) and 0.057 µg/L (10/28 - 11/24/12). None of the 7-day samples collected after the end of 2013 widespread use period from MSLO02 were selected for compositing into a 28-day sample; all 7-day samples were analyzed individually.

For the 7-day composite samples (47) collected at MSLO02 and analyzed individually, seven were reported below the LOD and 29 were reported below the LOQ and above the LOD. Of the remaining eleven, 7-day composite samples, four were collected in the summer of 2012 (7/1 - 7/28/12) and were reported at concentrations ranging from 0.0528 µg/L to 0.181 µg/L and two were collected in the fall of 2012 (weeks beginning 9/30/12 and 10/21012) and were reported at concentrations of 0.0541 µg/L and 0.067 µg/L, respectively. In 2013 two of the 7-day composite samples were collected during the summer weeks starting 6/30/13 and 7/14/13 and reported at concentrations of 0.0869 µg/L and 0.125 µg/L, respectively. In the fall of 2013, three samples collected during weeks starting 9/29/13, 10/13/13 and 10/20/13 were reported at concentrations of 0.0790 µg/L, 0.0584 µg/L, and 0.0594 µg/L, respectively.

Table 6 below shows the maximum concentration found at each site.

Table 6. Concentration of Methoxyfenozide in Surface Water in California, Mississippi and Michigan Lotic sites

Site	Maximum Concentration in Water-7 day composite (µg/L)	Maximum Concentration in Water-28 day composite (µg/L)	Range (µg/L)
California	1.01	0.589	ND-1.01
Mississippi	1.31	0.0588	ND-1.31
Michigan	ND	ND	--

LOQ=0.050 µg/L, LOD=0.015 µg/L, ND=not detected or below LOD

The methoxyfenozide results for sediment samples collected in all the lotic sites in the spring and fall of 2012 and 2013 were reported below the LOD (3.0 µg/kg) (p. 65 of the study report).

Lentic Sites

In California, the lentic site surface water samples were reported below the LOD (0.015 µg/L) for 17 of the 20 samples collected. The remaining three samples were reported at a concentration below the LOQ and above the LOD (refer to **Table 7** below and Table 19 p. 66 of the study report).

Methoxyfenozide results for lentic site surface water samples in Mississippi collected before the widespread use period were below the LOD for MSLE04 and reported at 0.0819 ug/L at MSLE05.

At the remaining three sites, concentrations were below the LOQ and above the LOD. Methoxyfenozide results for lentic site surface water samples in Mississippi collected after the 2012 widespread use period were reported below the LOD for MSLE01 and ranged from 0.0538 µg/L at MSLE04, to 0.0709 µg/L at MSLE05, to 0.233 µg/L at MSLE03. The result for MSLE02 was a concentration below the LOQ and above the LOD. Methoxyfenozide results for lentic site surface water samples in Mississippi collected before the 2013 widespread use period were below the LOD for MSLE01, MSLE02, and MSLE05. At the remaining two sites, concentrations were below the LOQ and above the LOD. For samples collected after the 2013 widespread use period were reported below the LOD for MSLE02, MSLE03, and MSLE04 sites. The result for MSLE01 was 0.0647 µg/L and the result for MSLE05 was at a concentration below the LOQ and above the LOD.

In Michigan, methoxyfenozide results for lentic site surface water samples collected before the widespread use period in 2012 were reported below the LOD for sites MILE02 and MILE05 and at concentrations of 0.845 µg/L, 0.0739 µg/L, and 0.369 µg/L for MILE01, MILE03, and MILE04, respectively. In 2013, results for samples collected before the widespread use period were reported below the LOD for sites MILE02 and MILE05 and at concentrations of 0.674 µg/L, 1.01 µg/L, and 0.570 µg/L for MILE01, MILE03, and MILE04, respectively. After the 2012 widespread use period, results were reported below the LOD for MILE05 and at a concentration of 0.0596 µg/L for MILE01 and at a concentration of 0.207 µg/L at MILE04. The MILE02 and MILE03 sites were at concentrations below the LOQ and above the LOD. Similarly, in 2013 the sample from MILE05 collected after the widespread use period was reported below the LOD (0.015 ug/L). The 2013 samples collected after the widespread use period from MILE01 through MILE04 were reported at 0.106 µg/L, 0.0789 µg/L, 0.302 µg/L, and 0.217 µg/L, respectively. The single sample collected from MILE06 (before the 2012 widespread use period) was reported at 0.398 µg/L. The replacement site, MILE07, was reported at 0.165 µg/L before the 2013 widespread use period and at concentrations below the LOQ and above the LOD after the widespread use period.

Table 7 shows the maximum values of all the monitored sites.

Table 7. Concentration of Methoxyfenozide in Surface Water in California, Mississippi and Michigan Lentic sites

Site	Maximum Concentration in Water from all the sites monitored (µg/L)	Range (µg/L)
California	0.0502	0.0167-0.0502
Mississippi	0.233	ND-0.233
Michigan	0.845	ND-0.845

LOQ=0.050 µg/L, LOD=0.015 µg/L, ND=not detected or below LOD

In California, methoxyfenozide results for all sediment samples collected during the four lentic site sampling events were reported below the LOD (3.0 µg/kg). Similarly, all 20 sediment samples collected over the 4 sampling events at the Mississippi lentic sites were reported below the LOD.

In Michigan, three detections of methoxyfenozide were reported for all of the Michigan lentic sediment samples. The spring 2013 sample for MILE03 was reported at 31.0 µg/kg. The remaining

three samples from MILE03 were reported below the LOD, along with all samples collected from MILE02 and MILE04. The spring 2013 sample collected from MILE01 was reported at below the LOQ and above the LOD. The remaining three samples from MILE01 were reported below the LOD. The single sample from MILE06, collected in the spring of 2012, was reported below the LOQ and above the LOD. Both samples collected at MILE07, collected in the spring and fall of 2013, were reported below the LOD.

III. Study Deficiencies and Reviewer's Comments

1. The study author did not explain why the 7- day samples were combined to make a 28-day composite.
2. The analytical methods was slightly modified: the samples were prepared with water:acetonitrile:formic acid (70:30:0.05) instead of 70:30:0.1 ratio as documented in the analytical method.
3. One sampling site was changed because the landowner filled the pond (MILE06) and therefore, an alternate sampling point was selected (MILE07).
4. Water samples were analyzed according to the analytical method described by DAS method 110356 (Shackelford, D. 2012). However, this method differs from the Environmental Chemical Method (ECM) in water and sediment submitted to the Agency and described in MRID 47824201 and 47809902, respectively.
5. Limited applications of methoxyfenozide were made during the two growing seasons monitored in Mississippi near the two lentic monitoring sites. In the fields surrounding the lotic sites and the MSLE01 site, applications to corn were made in both 2012 and 2013. Approximately 32.9 lbs a.i. were applied in two of the grower's blocks and 54.4 lbs a.i. were applied to five of the grower's blocks. In 2012, an application of 14.2 lbs a.i were made in two blocks at MSLE04. As a result, it is unclear as to how high the concentrations in surface water and sediment may have been if applications had been higher.

IV. References

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